

Question 1 (30 points)

Multiple choice questions: each question has 1 to 2 good answers; write your answers on answer sheet.

1.1 Concerning the standard entropy values of the following gases, the correct one(s) is:

- A · $SF_6 > SO_3 > SO_2 > O_3 > N_2 > H_2$ B · $H_2 > N_2 > O_3 > SO_2 > SO_3 > SF_6$
C · $SF_6 > SO_3 > O_3 > SO_2 > N_2 > H_2$ D · $O_3 > SO_2 > SF_6 > SO_3 > N_2 > H_2$

1.2 Which of the following description is not correct:

- A · covalent radius: $Co > Ni$, $Ni < Cu$ B · 1st ionization energy: $Si > P$, $P > S$
C · first electron affinity: $B > C$, $C < Si$ D · electronegativity: $O > Cl$, $O < F$

1.3 By dissolving 1.62 g of sulfur into 20 g of benzene, the boiling point of the benzene mixture increases by 0.81 K. Note that the modal boiling point elevation constant, $k_{b(\text{benzene})} = 2.53 \text{ kg} \cdot \text{mol}^{-1}$, what is the molecular formula of sulfur in the benzene mixture.

- A · S_2 B · S_4 C · S_6 D · S_8

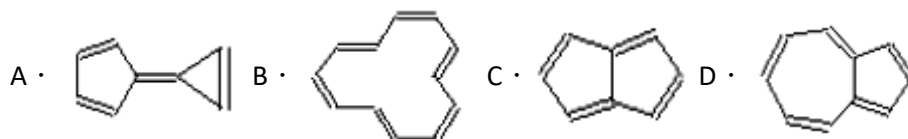
1.4 Of the following coordinative compounds, which one(s) has optical isomers:

- A · $[Pt(NH_3)_2(OH)_2Cl_2]$ B · $[Pt(NH_3)_2Cl_3(OH)]$
C · $[Co(NH_3)_2(en)_2]Cl_3$ D · $[Co(NH_3)(en)Cl_3]$

1.5 The number of isomers for chlorination of 3-methylpentane is (hint: consider also the stereoisomers)

- A · 6 B · 7 C · 8 D · 9

1.6 Which of the following molecules have aromaticity?



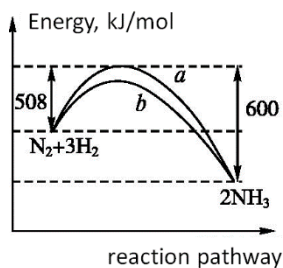
1.7 To distinguish starch solution from soap solution, which of the following test/solution does (do) not work?

- A. iodine solution B. diluted nitric acid C. pH paper D. NaOH

1.8 Referring to the diagram below, it shows the variation of energy during the course of a chemical reaction for N_2 and H_2 . The correct description is:

- A · the chemical reaction and reaction enthalpy is $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = -92 \text{ kJ} \cdot \text{mol}^{-1}$
B · curve *a* depicts the energy change when a catalyst is used.
C · by the addition of a catalyst, the value of reaction enthalpy changes.

D · when the temperature and volume remain constant, the addition of 1 mol of N_2 and 3 mol of H_2 results in the heat release of Q_1 kJ. If 2 mol of N_2 and 6 mol of H_2 are added, the heat release is Q_2 kJ. That is $184 > Q_2 > 2Q_1$.



1.9 The working principle for the portable device used for alcohol consumption detection is based on a fuel cell. Under acidic condition, ethanol can, in theory, be completely oxidized to CO_2 . In practice, only **X** amount of ethanol is oxidized. The reaction that happens in one of the electrodes is as follows: $CH_3CH_2OH - 2e^- \rightarrow X + 2H^+$; the following description(s) that is correct includes

- A · H^+ ions moves from anode to cathode in the fuel cell;
- B · the chemical reaction in the other electrode is: $O_2 + 4e^- + 2H_2O \rightleftharpoons 4OH^-$;
- C · reaction involving ethanol occurs in anode, electrons pass into anode through external circuit;
- D · the overall cell reaction is: $2CH_3CH_2OH + O_2 \rightarrow 2CH_3CHO + 2H_2O$

1.10 By adding an appropriate amount of $AgBr$ solid, an equilibrium $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ is established. The following description(s) that is correct includes

- A · adding sufficient drops of concentrated $NaCl$ (aq), yellow solid turns white in the system; this implies $K_{sp}(AgCl) < K_{sp}(AgBr)$
- B · adding a small quantity of $AgBr(s)$ to the system, when the equilibrium re-establishes itself, $c(Ag^+)$ and $c(Br^-)$ both increase.
- C · in the equilibrium, there exists $c(Ag^+) = c(Br^-) = \sqrt{K_{sp}(AgBr)}$.
- D · if in a certain solution, $c(Ag^+) \cdot c(Br^-) = K_{sp}(AgBr)$, then it follows that $c(Ag^+) = c(Br^-)$.

1.11 The following compounds react with hydrogen chloride via oxidative addition reaction. The product which is unstable is:

- A · $IrCl(CO)(PPh_3)_2$
- B · $IrPh(CO)(PMe_3)_2$
- C · $IrMe(CO)(PMe_3)_2$
- D · $IrCl(CO)(PMe_3)_2$

1.12 Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, is often used as the standard reference in acid-base titration. The relation(s) which is not correct is:

- A · $c(\text{SO}_4^{2-}) > c(\text{NH}_4^+) > c(\text{Fe}^{2+}) > c(\text{H}^+) > c(\text{OH}^-)$ B · $c(\text{SO}_4^{2-}) = c(\text{NH}_4^+) > c(\text{Fe}^{2+}) > c(\text{H}^+) > c(\text{OH}^-)$
 C · $c(\text{H}^+) = c(\text{OH}^-) + c(\text{NH}_3 \cdot \text{H}_2\text{O})$ D · $2c(\text{SO}_4^{2-}) + c(\text{OH}^-) = c(\text{NH}_4^+) + 2c(\text{Fe}^{2+}) + c(\text{H}^+)$

1.13 The oxidative property of a substance is related to its concentration. When either hydrogen ions or hydroxide ions are involved in a chemical reaction, the relative acidity significantly influences its oxidative property. In the following reactions, the rise in acidity that does not favor the products is:

- A · Chlorine oxidizes Fe(III) to FeO_4^{2-} B · CoF_3 oxidizes Mn^{2+} to MnO_4^-
 C · Fe^{3+} oxidizes Cu to Cu^{2+} D · chlorine gas is made from reaction of Mn(IV)oxide and conc. HCl

1.14 For a chemical reaction at $t^\circ\text{C}$, the equilibrium constant is expressed as, $K = \frac{c(\text{NO}) \cdot c(\text{SO}_3)}{c(\text{NO}_2) \cdot c(\text{SO}_2)}$. At constant volume, when temperature increases, the concentration of NO decreases. The description that is correct is:

- A · the entropy of the reaction is positive.
 B · at constant temperature, when the pressure drops, the reaction system appears more intense in color.
 C · when temperature increases, the rate of reverse reaction increases.
 D · the chemical reaction is: $\text{NO}_2 + \text{SO}_2 \rightleftharpoons \text{NO} + \text{SO}_3$

1.15 X is a metal, which has just one electron in its outer shell. When X reacts with hydrochloric acid, a blue substance, Y, is formed. As soon as Y is form, it is oxidized to a green solution, Z. When excessive KOH is added to Z, large amount of precipitate appears, that is followed by its dissolution to form V; the addition of hydrogen peroxide to V leads to the color of solution gradually fading to yellow; by heating, excess hydrogen peroxide is removed, that is followed by the addition of hydrochloric acid to adjust the pH to acidic. The solution gradually turns orange-red, forming W, which is used to test the presence of ethanol. If hydrogen peroxide is added to this solution, it will first turn the solution to blue, reforming Z. The following description about X that is correct is:

- A · X is a very hard substance. B · under acidic condition, W and ethanol can react to form Z.
 C · X is an alkaline metal. D · X and peroxide react to form a blue substance Y.

Question 2 (10 points)

Based on the information provided, write the corresponding ionic equation for the following reactions.

2.1 $\text{KMnO}_4(\text{aq})$ is added $\text{SnCl}_2(\text{aq})$ acidified by sulfuric acid to completion.

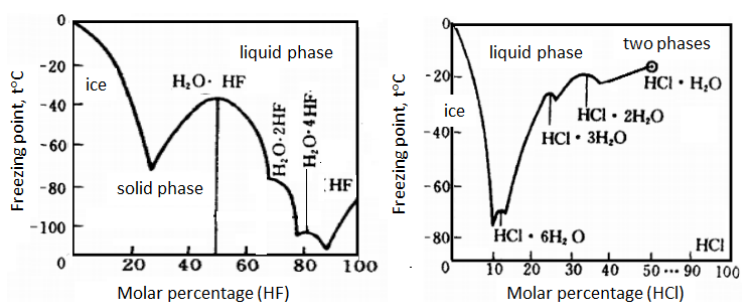
2.2 In basic solution, H_2O_2 is added to $\text{Fe}(\text{CN})_6^{3-}$ to form $\text{Fe}(\text{CN})_6^{4-}$.

- 2.3 When chromium hexacarbonyl reacts with N_2O_5 , a green nitrate salt is precipitated while two gases are emitted.
- 2.4 In 100% H_2SO_4 , I_2 (7 mol) + HIO_3 (1 mol) + H_2SO_4 (8 mol) form 16 mol of ions.
- 2.5 When molybdenite (MoS_2) and oxygen react in alkaline solution, molybdate and sulfate ions are formed.

Question 3 (7 points)

Liquid HF is an excellent solvent for the ionic type of substance, as it has a strong Lewis acidity and a relatively high electric permittivity.

- 3.1 When LiF is dissolved in HF, two types of ions are formed: briefly describe the causes for this chemical reaction.
- 3.2 Perchloric acid appears as amphoteric in HF. Write down the two chemical reaction equations.
- 3.3 The hydrate mixture for HF and HCl is shown in the following diagram. (The melting points for HF and HCl are -83.4°C and -114.7°C , respectively)

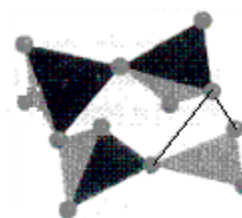


Compare and explain the forms how HF and HCl exist in water.

Question 4 (12 points)

Vanadate exists in various ionic form in aqueous solution, for examples, as VO_4^{3-} , $\text{V}_2\text{O}_7^{4-}$, $\text{V}_3\text{O}_{10}^{5-}$, etc.

- 4.1 Write the structural formula for the following ions: VO_4^{3-} , $\text{V}_2\text{O}_7^{4-}$, and $\text{V}_3\text{O}_{10}^{5-}$
- 4.2 Vanadium crystal belongs to cubic cell, in which the nearest nuclear distance between metal atoms is 262.0 pm, the next closest distance is 302.5 pm. Please calculate the maximum radius which can fit into the gaps within the vanadium crystal lattice.
- 4.3 The tetrahedron with a neutral quadratic ring formed with manganese, vanadium, and oxygen atoms is shown in following figure. The ratio of manganese and vanadium atoms in the tetrahedron is 1:3. An ethylenediamine (en) molecule can be inserted into the ring through multiple hydrogen bonds. Write down the (chemical) formula after an insertion of en.



- 4.4 $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is a new type of material for lithium based anode. Their cations with two types of polyhedron combine to form 3-dimensional network structure. Please write the bonding connection for all the atoms of the cations.

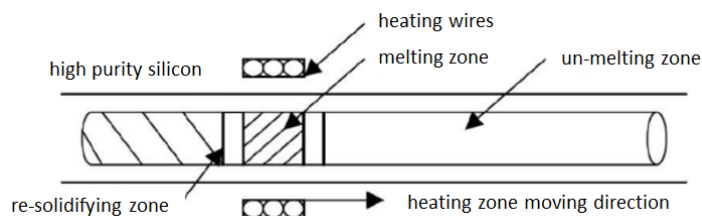
Question 5 (8 points)

Ultrahigh purity silicon is the major material for semiconductor manufacturing. Chemical processing is usually the first step to obtain the higher purity silicon, followed by physical processing to obtain ultrahigh purity.

- 5.1 Processed at 300°C , raw silicon powder is reacted with HCl to form 1 mol $\text{SiHCl}_3(\text{g})$ and H_2 , releasing 225 kJ as heat. Please draw the three-dimension structure for SiHCl_3 , indicating the direction of dipoles. And write the thermochemical equation.

5.2 Silane is a colorless gas, readily decomposed, and can be used to prepare high purity silicon. Using SiO_2 as the starting materials, it is used in non-aqueous-based ether to prepare SiH_4 . Other reactants include LiAlH_4 and some common inorganic compounds. Using this method, please write the stepwise reaction equations.

5.3 During the manufacturing of the ultra-high purity silicon, the last step involves the zone melting/refining; which is a process repeated until the impurity measured below 0.1 ppb (ppb = part per billion).



As impurity reaches above 0.1 ppb, calculate the amount of silicon being substituted by impurity, in terms of per gram of silicon.

5.4 The electrical conductivity of ultra-pure silicon is quite poor. Additives can be added to improve its conductivity. After the addition, the electrical carrier changes to a semiconductor-type. Please explain the principle how a tiny quantity of boron (B) which substitute silicon works in the semiconductor. State the type of resultant semiconductor.

Question 6 (6 points)

The quantity of barium carbonate can be determined by iodometric titration. A sample of 0.1250 g was dissolved and added to excess amount of $\text{K}_2\text{Cr}_2\text{O}_7$ in neutral condition. After the complete sedimentation, the precipitate was rinsed. A certain amount of hydrochloric acid is then added to dissolve the precipitate. It was followed by the addition of excess amount of KI . Subsequently, the resultant mixture was left in dark for 5 minutes. Afterward, NaHCO_3 was added with water to dilute. The solution mixture was then titrated against $\text{Na}_2\text{S}_2\text{O}_3$ [$\text{c}(\text{Na}_2\text{S}_2\text{O}_3)$ is equivalent to 1.00 mL of 0.01250 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$], using starch as the indicator. The titration was stopped when the blue solution turned colorless. The total volume used in titration is 25.50 mL ($\text{Na}_2\text{S}_2\text{O}_3$).

6.1 Write the major ionic reaction equations involved in this quantitative analysis.

6.2 Calculate the weight % (mass) of BaCO_3 in the sample. Note that $\text{MR}(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 249.68 \text{ g/mol}$, $\text{MR}(\text{BaCO}_3) = 197.31 \text{ g/mol}$.

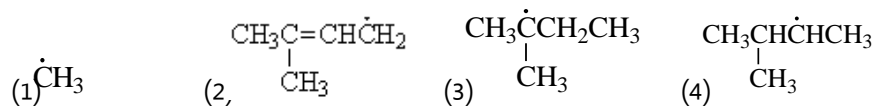
Question 7 (5 points)

When metallic lithium is used in ether to react with $\text{Co}_2(\text{CO})_8$, a red crystalline solid Li^+R^- is obtained, and carbon monoxide is emitted. In the infrared spectrophotogram, the crystalline solid has three different carbonyl group in its vibration-absorption peaks, at $2080 \sim 2000 \text{ cm}^{-1}$, 1850 cm^{-1} , and 1600 cm^{-1} . The Co content in the anion R^- is 0.387; in addition, several Co atoms lie on a plane through metal-metal connection. Each Co atom satisfies effective atomic number (EAN) rule.

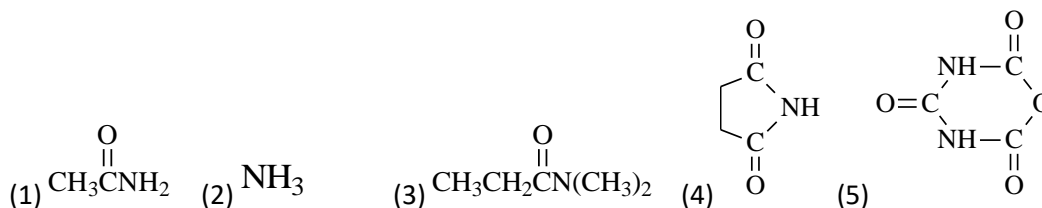
Write the anion formula and draw its spatial structural formula.

Question 8 (6 points)

8.1 Arrange the following radicals in the order of relative stability: _____



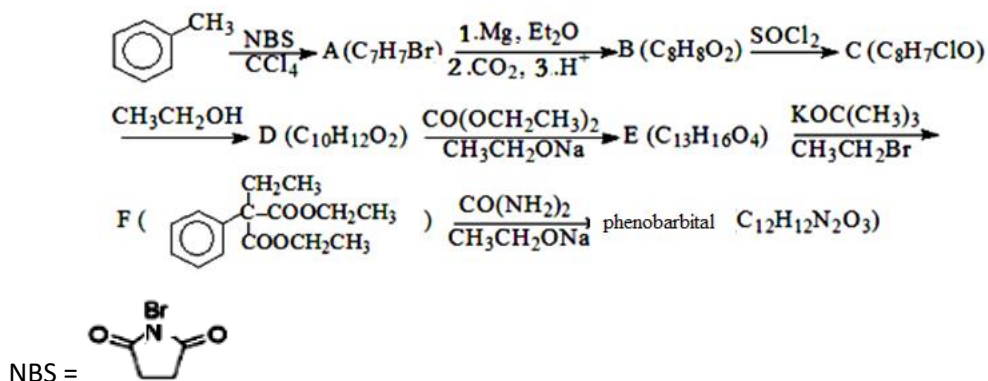
8.2 Arrange the following amines according to their alkaline strength: _____



8.3 As alkynes can be mono-halogenated, it can also be bi-halogenated. However, this process is relatively more difficult to occur compared to that of alkenes; the reaction rate is also slower correspondingly. Please explain why this is the case.

Question 9 (10 points)

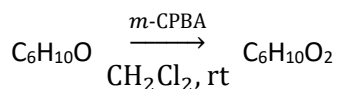
Under the law, anti-convulsion drugs, sedative, such as phenobarbital, is prohibited from adding to pig's feedstock. In addition, using sedative such that pigs sleep more and exercise less does not necessarily accelerate pig's growth. Under normal circumstances, bred pig lives in very restricted areas. It is therefore not essential to use sedatives. The synthetic route of phenobarbital is shown as follows:



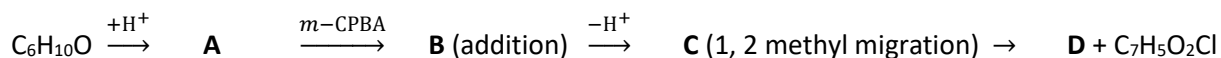
- 9.1 Write the systematic name for NBS _____
- 9-2 The function(s) of NBS in the phenobarbital synthesis is _____
- (A) catalyst (B) oxidizing agent (C) targeted bromine substituting agent
(D) initiator for polymerization
- 9-3 Please write the structural formula for the compounds **A** to **E**, and that of phenobarbital.

Question 10 (6 points)

Cyclohexane can be oxidized by meta-chloroperoxybenzoic acid (*m*-CPBA):



The reaction mechanism is partially shown as follows:



Identify A, B, C, and D, showing structural formula. (note: curly arrow is required for the process between B and C)

~ end ~